

(2) Polymerization of the K^+ and Rb^+ salts of acrylic acid proceeds easily at room temperature, while the Li^+ and Na^+ salts have to be heated to about $150^\circ C$. to achieve comparable rates. Since the acrylate ion is the reactive species in all these cases, the cation can affect the rate only because it determines the nature of the crystal lattice. There is also a very large difference between the reactivities of the potassium salts of acrylic and methacrylic acid, although the intrinsic reactivity of the monomer should be very similar.

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An Improved Chromatographic System for the Extraction-Precipitation Fractionation of Polymers

The new chromatographic procedure of Baker and Williams,¹ in which each stage of the column corresponds to a fractional extraction and precipitation step, appears to be the most promising column method for the fractionation of polymers. The method depends upon the combined use of a solvent gradient, supplied by the usual mixing vessel and reservoir system, and a thermal gradient along the column, maintained by an aluminum jacket which is heated at the top and cooled at the bottom. In working with the set-up used by Baker and Williams, it was found that certain mechanical problems made it difficult to achieve the degree of control required in our studies. In particular, leakage of solvents from the glass joints connecting the various components of the system made it difficult to control the solvent gradient or rate of flow of solvent through the column. Another problem was the release of dissolved air from the solvents passing through the heated zone at the top of the column. The released air, about 1 cc./15 cc. of solvent, disrupted the packing of the column and collected in the mixing vessel causing a continuous shift from a predetermined solvent gradient. This note describes improvements in the column design which eliminate these difficulties and lead to better control over variables that may affect the fractionation.

Figure 1 shows the essentials of a modified chromatographic system which has been operated successfully with a column 2.5 cm. in diameter, corresponding to the dimensions of Baker and Williams' column, as well as with 4 and 6 cm. diameter columns. All ground glass joint connections have been eliminated. The connection between the mixing vessel and the column is made with glass pipe fittings, designated by PF, using an interface gasket of Teflon. A nylon union for $1/4$ " outside diameter tubing (available from

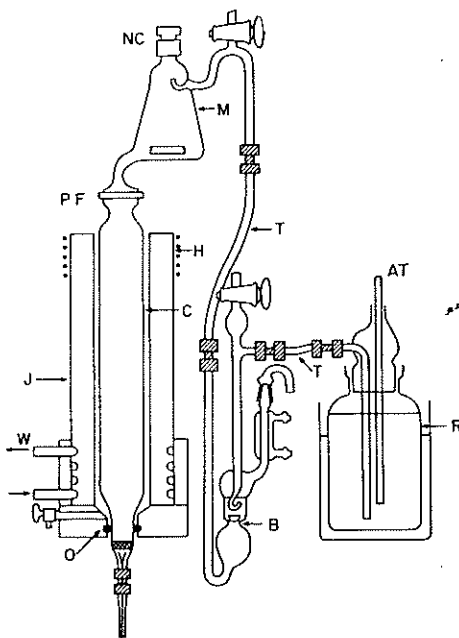


Fig. 1. Modified chromatographic system.

Crawford Fitting Co., Cleveland, Ohio) is used to connect the capillary to the column as well as for various other connections in the system as shown in Figure 1 by the shaded items. Unions of this type are reusable, operate smoothly, and make a tight fit on glass as well as on flexible tubing of the proper size. If nylon is objectionable, a brass union may be used with a Teflon sleeve which fits over the glass tubing.

The redesigned mixing vessel (M) is open at the top so that it can be filled with heated, air-free solvent and then sealed with a nylon cap (NC) which fits 1/2" outer diameter tubing. The reservoir operates on the principle of a Mariotte bottle to maintain a constant level in the small boiling flask (B). As the solvent from the reservoir passes through the boiling flask it is purged of air before it enters the mixing vessel. A perforated Teflon chip at B, suspended on glass indentations in the boiling flask, produces uniform boiling and may be regenerated by drying. To supply a convenient degree of flexibility to the system, a short length of polyethylene or Teflon tubing (T) is used to connect the reservoir with the boiling flask and the boiling flask with the mixing vessel. This arrangement of the boiling flask as a leveling bulb reduces the effective head of liquid in the column so that a larger diameter capillary tip may be used in controlling the flow rate to avoid any stoppage at this point.

Two other differences from the Baker and Williams system deserve mention. The thermal contact with copper cooling coils wrapped around the lower end of the jacket was found to be inadequate. Therefore, the cooling water, supplied by a circulating refrigeration bath, is carried through a helical groove cut into the wall of the jacket and sealed with a press fitted sleeve as shown in Figure 1. In addition, to improve heat transfer between the jacket and the column, the jacket was fitted with an O-ring gland at O. The glass column tapers at the bottom to a piece of selected tubing which fits the O-ring properly so that the space between the jacket and column can be filled to the top of the jacket with mineral oil. For certain experiments the column was heavily in-

ulated and temperature regulation was improved by operating the heating coils from a Variac supplied by an electronic voltage regulator and by controlling the refrigeration bath with a sensitive mercury thermoregulator.

With the improvements described here, this system offers good control over variables which may be important for fractionation. The aluminum jacket surrounding the column offers better temperature control and a more linear thermal gradient than can be obtained by heating the glass column directly. Control of the flow rate by a capillary makes it possible to produce the slow flow rates which may be necessary for fractionation at high molecular weights. The column operates as a closed system and, if the mixing vessel remains filled and there is no leakage, a simple mixing equation is applicable to determine the composition of the eluting solvent and establish its relation to molecular weight.

The system has given satisfactory results with polystyrene over a large range of molecular weights and has proven capable of a high degree of reproducibility and resolution. For example, a 0.4-g. sample of Dow Styron, $MW = 5 \times 10^5$, was fractionated on a 4-cm. diameter column and a 2-g. sample was fractionated on a 6-cm. diameter column. The resulting integral distribution curves from these two runs coincided to a weight fraction of 0.9 where the molecular weight was 1.2×10^6 and differed only slightly beyond this point. Additional details of this fractionation and work in progress on the effect of certain variables on the fractionation results will be reported in future communications.

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The Polymerization of Ethylene with the Monocyclopentadienyl Titanium Trichloride-Triethylaluminum Complex as the Catalyst

It has recently been reported by Natta and co-workers¹ that the complex formed by the reaction of bis(cyclopentadienyl)titanium dichloride and triethylaluminum acts as a catalyst for the polymerization of ethylene. Breslow and Newburg² have also shown that $(C_5H_5)_2TiCl_2$ in conjunction with diethylaluminum chloride has even greater catalytic activity for the low temperature and low pressure polymerization of ethylene when the monomer contains trace amounts of oxygen. The synthesis of monocyclopentadienyl titanium trichloride^{3,4} by Sloan and Barber of these Laboratories led to the present investigation.

It has been found that the product of the reaction between $C_5H_5TiCl_3$ and $Al(C_2H_5)_3$ is a catalyst for the polymerization of ethylene at room temperature and atmospheric pressure if HCl is added to the reaction medium. As shown in Table I, the activity of the catalyst is also dependent on the mole ratio of $Al(C_2H_5)_3:C_5H_5TiCl_3$ and the con-

centration of oxygen in the monomer. The most active catalyst was obtained at a mole ratio of 2.5-3.14 and at an oxygen concentration of 440 p.p.m.

TABLE I

| | Experiment no. | | | | | | |
|---|----------------|------|------|------|------|-------|------|
| | 37 | 45 | 48 | 50 | 51 | 53 | 49 |
| Mmoles $C_2H_5TiCl_2$ | 2 | 2 | 1 | 0.78 | 0.70 | 0.484 | 1 |
| Mmoles $Al(C_2H_5)_3$ | 6.28 | 6.28 | 3.14 | 1.95 | 0.84 | 3.39 | 3.14 |
| Mole ratio $AlR_3/RTiCl_2$ | 3.14 | 3.14 | 3.14 | 2.5 | 1.2 | 7.0 | 3.14 |
| Mmoles HCl | — | 5 | 2.5 | 1.55 | 0.70 | 1.43 | 2.5 |
| O ₂ concentration, p.p.m. | 440 | 12 | 440 | 440 | 440 | 440 | 900 |
| Solid polyethylene, g. | 0.04 | 1.4 | 6.5 | 6.6 | 0.15 | 0.10 | 3.8 |
| M.p., °C. | | | 133 | 134 | | | 134 |
| η_{sp}/c^a | | | 1.17 | 1.19 | | | 1.29 |

^a Reduced viscosity, 0.203 g. polymer in 100 ml. tetralin at 135°C.

The catalyst was prepared by dissolving the desired amount of the yellow $C_2H_5TiCl_2$ in 150 ml. dry, degassed benzene under a pure nitrogen blanket in an all-glass reactor followed by the dropwise addition of the $Al(C_2H_5)_3$ in benzene (30% solution). The yellow solution turned black immediately after the addition of the $Al(C_2H_5)_3$. After stirring for 20 minutes at room temperature, ethylene was bubbled through this reaction medium. Ten minutes later, the HCl in benzene solution (ca. 0.3 *N*) was added to the reactor. The ethylene flow was continued for five hours at a rate slightly greater than that at which it was being absorbed. In the experiments where the catalytic activity was highest (No's 48 and 50), a 10°C. increase in temperature had occurred at the end of five hours and the reaction mixture had turned light brown. The polymer was isolated as a white powder by adding 100 ml. of methanol to the reactor, filtering off the solids, washing with methanolic HCl and methanol, and finally drying to constant weight *in vacuo*.

From the high, sharp melting points and the viscosity data, it is evident that the polyethylene produced with the $C_2H_5TiCl_2$ - $Al(C_2H_5)_3$ -HCl catalyst system is comparable to the Ziegler-type product.

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